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(54) Title: A NON-LIQUID FATTY PRODUCT CONTAINING WATER AND AT LEAST ONE POLYUNSATURATED FATTY ACID AND A PROCESS FOR THE PRODUCTION OF SAME

(57) Abstract

A non-liquid fatty product containing an inert gas, at least one polyunsaturated fatty acid, water and optionally an antioxidant and a process for the production of same wherein an inert gas is whipped into an emulsion wherein the oil phase is initially softened by heating which oil phase contains at least 1 percent by weight of a polyunsaturated fatty acid of the n-3 series comprising at least four double bonds or at least 0.5 percent by weight of a polyunsaturated fatty acid of the n-6 series comprising at least three double bonds and wherein the emulsion contains at least 1 percent by weight of oxygen-deficient water. Thus, protection of the fatty product against oxidation is accomplished and at the same time a suitable texture is imparted thereto.

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# A NON-LIQUID FATTY PRODUCT CONTAINING WATER AND AT LEAST ONE POLYUNSATURATED FATTY ACID AND A PROCESS FOR THE PRODUCTION OF SAME.

## BACKGROUND OF THE INVENTION.

The present invention relates to a non-liquid fatty product containing an inert gas, at least one polyunsaturated fatty acid, water, and optionally an antioxidant.

In a known process (Gillies, M.T., Shortenings, Margarines and Food Oils, Noyes Data Corporation, New Jersey, 1974, 333 pp.) for the production of a optionally foamy fatty product of the kind described above (e.g. various types of shortening and whipped margarine) air or an inert gas is whipped into a heated liquid fat or liquid water-in-oil emulsion.

Thus, subsequent to suitable cooling and kneading a product having a soft texture at low temperatures (0°C-5°C) is obtained. Moreover, the whipping of air into fats for use as shortening serves to impart to the product an opaque, margarine-like appearance. The whipping of air or inert gas into margarine is effected in order to improve the frying properties and the organoleptic properties of the margarine and to protect it from the formation of mould.

Apart from being used for baking and frying, margarine is used as a spread and for this particular purpose it is often produced from oils containing polyunsaturated fatty acids which essentially consist of linoleic acid comprising two double bonds (18:2 n-6) and which less frequently have a low content of α-linolenic acid comprising three double bonds (18:3 n-3).

A disadvantage of the disclosed water-in-oil emulsion is that oxygen is introduced into the fatty product in the water phase. Dissolved oxygen in the water phase reduces the shelf life of fatty products containing polyunsaturated fatty acids considerably, because polyunsaturated fatty acids having more than two double bonds are very easily oxidized, and the existing technology does not disclose how to produce a margarine emulsion in an oxygen-deficient environment. Thus, up till now, it has been impossible to produce a non-liquid fatty spread having a long shelf life and an increased content of polyunsaturated fatty acids of the n-3 series comprising at least 4 double bonds or of

the n-6 series comprising at least 3 double bonds.

This is unfortunate since a series of tests carried out in the past 20 years or so (Dyerberg, J., Linolenate-derived Polyunsaturated Fatty Acids and Prevention of Atherosclerosis, Nutrition Reviews, vol. 44, No. 4, 1986, pp 125-134) have shown that a daily intake of a few grammes of i.a. polyunsaturated fatty acids comprising 5 double bonds (20:5 n-3 and 22:5 n-3), which are mainly present in marine oils, particularly fish oils, and in phyto-plankton and algae, reduces the cholesterol content of the blood and the risk of developing heart and vascular disorders by virtue of their conversion into the physiologically active prostaglandin $E_3$ ($PGE_3$).

The intake of linoleic acid (18:2 n-6) alone, which has two double bonds and which is converted slowly in the organism into the physiologically active prostaglandins $PGE_1$ and $PGE_2$, is frequently not sufficient to obtain a corresponding effect because the first step which comprises the conversion of linoleic acid into γ-linolenic acid is catalysed by the enzyme δ-6-desaturase which frequently has low activity in man (Hassam, A.G., The Role of Evening Primrose Oil Nutrition and Disease., Jn: The Role of Fats in Human Nutrition, Ellis Horwood Limited, Chicester, 1985, pp 84-100). γ-Linolenic acid (18:3 n-6), which is present in vegetable oils such as evening primrose oil, borage oil and black-currant seed oil, is therefore a more efficient precursor in the biosynthesis of $PGE_1$ and $PGE_2$ (Gurr, M.J., Role of Fats in Food and Nutrition, Elsevier Applied Science Publishers, London New York, 1984, 170 pp), and this fact has led to a growing interest in the use of γ-linolenic acid in i.a. food products.

However, it has not been possible to use commercially an amply occuring raw material, such as fish oil and in particular sand eel oil having a high content (about 15 percent by weight to about 30 percent by weight) of n-3 fatty acids and vegetable oils, such as the above mentioned, having a high content (about 14 percent by weight to about 33 percent by weight) of n-6 fatty acids, in their unhydrogenated state for the sake of the shelf life thereof, and thus the desirable nutritive and wholesome effects thereof have not been fully utilized.

It is the object of the present invention to produce a stable and phy-

siologically active fatty product of the kind described above.

This object is achieved with the fatty product of the invention, which is characterized in that it is a water-in-oil emulsion or an oil-in-water emulsion containing at least 1 percent by weight of oxygen-deficient water and wherein the oil phase contains at least 1 percent by weight of a polyunsaturated fatty acid of the n-3 series comprising at least four double bonds and/or at least 0.5 percent by weight of a polyunsaturated fatty acid of the n-6 series comprising at least three double bonds. The water is rendered oxygen-deficient by e.g. sparging with inert gas, boiling out or by naturally containing inert gas.

By oxygen-deficient is understood that the amount of dissolved oxygen in the used water or water phase for the product of the invention is not sufficient to cause any substantial oxidation of the polyunsaturated fatty acids contained in said product.

It is surprisingly found that the highly unsaturated fatty acids are stabilized in a fatty product wherein the water phase is oxygen-deficient and into which inert gas and optionally a suitable amount of antioxidants have been whipped, thus imparting to the final product a peroxide number according to the IUPAC (2.501) of less than about 1 meq/kg.

Furthermore, the addition of preservatives, such as potassium sorbate, and antioxidants, such as alkylgallates, ascorbyl fatty acid esters and tocopherols, affords further improvement of the durability of the products according to the invention and, additionally, the antioxidants also aid in the protection of the fatty acids against oxidation occurring in the organism.

In one preferred embodiment of the invention mineral water, which is naturally carbonized water, is used for the water phase, which may further contain salt, flavours, milk solids, and thickeners, such as gelatin, alginate, and guar gum. An emulsion is prepared by adding the water phase to a mixture of heated fats and oils containing an emulsifier, such as a monodiglyceride of a fatty acid or a lecithine, and subsequently whipping the emulsion with an inert gas in an oxygenfree atmosphere. The whipped emulsion, which is of margarine type, is cool-

ed and packed.

In fatty products of the invention consisting of a water-in-oil emulsion the solid fat proportion at the storage temperature of the total fat and oil content is preferably not less than 10 percent by weight in order to obtain a non-liquid product and retain the whipped-in inert gas. Alternatively the oil phase can be reduced by using a suitable amount of thickener and/or gelling agent to obtain a non-liquid product.

In another preferred embodiment of the invention an oil-in-water emulsion is prepared by adding oil to a mixture of $N_2$-sparged water and emulsifier. Vinegar may finally be added to obtain a mayonnaise-like product, which preferably is packed in air-tight containers.

For products of the invention consisting of an oil-in-water emulsion, such as mayonnaise, wherein the oil raw material is liquid at storage temperature, no solid fat is necessary in order to retain the whipped-in inert gas.

A preferred content of inert gas, such as $N_2$, in the fatty product corresponds to 15 percent by volume.

The invention further relates to a process for the production of a non-liquid fatty product containing an inert gas, at least one polyunsaturated fatty acid, water and optionally an antioxidant, wherein the inert gas is whipped into an oil-in-water emulsion or a water-in-oil emulsion wherein the oil phase comprises a mixture of fatty substances which was initially softened by heating and wherein the product thus produced is cooled. The process is characterized in using a mixture of fatty substances containing at least 1 percent by weight of a polyunsaturated fatty acid of the n-3 series comprising at least four double bonds and/or at least 0.5 percent by weight of a polyunsaturated fatty acid of the n-6 series comprising at least three double bonds and at least 1 percent by weight of oxygen-deficient water.

The products produced in the process according to the invention may be packaged like similar products containing polyunsaturated fatty acids

comprising two double bonds and having a low content of polyunsaturated fatty acids comprising three or more double bonds.

In the following examples the invention will be described in further detail.

Example 1

A water phase (10 percent by weight of mineral water (naturally carbonized water)), 0.02 percent by weight of flavouring 2807, and antioxidants (propylgallate 100 ppm, ascorbylpalmitate 43 ppm, α-tocopherol 1000 ppm) is added while stirring to a preheated (40°C-80°C) mixture of 89.6 percent by weight of fat blend (10 parts soya m.p. 41°C, 40 parts soya m.p. 35°C, 30 parts soya oil, and 20 parts fish oil), 0.2 percent by weight og soya lecithin, 0.2 percent by weight of DIMODAN PV (mono- and diglyceride emulsifier) and 0.02 percent by weight of flavouring 3090. The water-in-oil emulsion having a temperature of about 45°C is then cooled to 4°C by passage through a one-pipe pilot plant of the Gerstenberg and Agger type. Gaseous nitrogen is introduced into the suction part of the high-pressure pump via a distribution nozzle to obtain a final product having a nitrogen content of 15 percent by volume. The product is filled into cups immediately upon the pipe cooler treatment. The final product is stored at a maximum temperature of 10°C.

The fatty acid composition of the fish oil is as follows:

| Fatty acid | percent by weight |
|---|---|
| C 14:0 | 8.0 |
| C 15:0 | 0.3 |
| C 16:0 | 17.4 |
| C 16:1 | 9.5 |
| C 16:2 | 0.6 |
| C 18:0 | 1.2 |
| C 18:1 | 9.1 |

| Fatty acid | percent by weight |
|---|---|
| C 16:4 | 0.5 |
| C 18:2 | 1.9 |
| C 18:3+20:1 | 8.9 |
| C 18:4+n-3 | 3.9 |
| C 22:1 | 13.3 |
| C 20:4 n-3 | 0.7 |
| C 20:5 n-3 | 10.5 |
| C 24:1 | 1.6 |
| C 22:4 | 0.8 |
| C 22:5 n-3 | 0.8 |
| C 22:6 n-3 | 9.4 |

In an accelerated storage experiment this product was stored at 25°C for 4 weeks without developing any off-flavour. The peroxide number was below 1 meq/kg after 4 weeks. In Denmark the accepted maximum period of storage for vegetable oil margarines is 7 weeks at temperatures below 10°C.

Example 2

A water phase (10 percent by weight of boiled mineral water, 0.02 percent by weight of flavouring 2807, and antioxidants (propylgallate 100 ppm, ascorbylpalmitate 43 ppm, α-tocopherol 1000 ppm) is added while stirring to a preheated (40°C-80°C) mixture of 89.6 percent by weight of fat blend (10 parts soya m.p. 41°C, 40 parts soya m.p. 35°C, 30 parts soya oil, and 20 parts fish oil), 0.2 percent by weight of soya lecithin, 0.2 percent by weight of DIMODAN PV (mono- and diglyceride emulsifier) and 0.02 percent by weight of flavouring 3090. The water-in-oil emulsion having a temperature of about 45°C is then cooled to 4°C by passage through a one-pipe pilot plant of the Gerstenberg and Agger type. Gaseous nitrogen is introduced into the suction part of the high-pressure pump via a distribution nozzle to obtain a final product having a nitrogen content of 15 percent by weight. The product is filled into airtight plastic cups immediately upon the pipe cooler treatment. The final product is stored at a maximum temperature of

10°C.

The fish oil had the same composition as in Example 1.

In an accelerated storage experiment this product was stored at 25°C for 4 weeks without developing any off-flavour. The peroxide number was below 1 meq/kg after 4 weeks. In Denmark the accepted maximum period of storage for vegetable oil margarines is 7 weeks at temperatures below 10°C.

Example 3

A mayonnaise-type product is produced from the following ingredients:

| Ingredients | Percent by weight | |
|---|---|---|
| Fish Oil* | 10,0 | * same composition as in Examples 1 and 2. |
| Rapeseed oil | 70,0 | |
| Vinegar | 1,5 | |
| Egg yolks | 4,0-6,0 | |
| Thickener | 0,3 | |
| Salt | 0,3 | |
| Flavour | 0,02 | |
| Water, preservatives, etc., up to | 100 | |

Mineral water is poured into a mayonnaise plant, emulsifying turbine, or the like and egg yolks are added. Then the oil including dispersed thickener, salt, and preservatives are added continuously. Finally vinegar is added. The product is whipped with inert gas before being packaged in air-tight bottles.

In an accelerated storage experiment this product was stored at 25°C for 4 weeks without developing any off-flavour.

Claims

1. A non-liquid fatty product containing an inert gas, at least one polyunsaturated fatty acid, water and optionally an antioxidant, characterized in that the fatty product is a water-in-oil emulsion or an oil-in-water emulsion containing at least 1 percent by weight of oxygen-deficient water and wherein the oil phase contains at least 1 percent by weight of a polyunsaturated fatty acid of the n-3 series comprising at least four double bonds and/or at least 0.5 percent by weight of a polyunsaturated fatty acid of the n-6 series comprising at least 3 double bonds.

2. A fatty product according to claim 1, characterized in that it comprises at least 1 percent by weight of a polyunsaturated fatty acid of the n-3 series comprising 5 double bonds, preferably eicosapentaenoic acid (10:5 n-3).

3. A fatty product according to claim 1, characterized in that it comprises at least 0.5 percent by weight of a polyunsaturated fatty acid of the n-6 series comprising at least three double bonds, preferably γ-linolenic acid (18:3 n-6).

4. A fatty product according to claim 1, characterized in that it contains from about 10 percent by weight to about 85 percent by weight of refined fish oil.

5. A fatty product according to claim 1, characterized in that it comprises a water-in-oil emulsion in which the water phase constitutes from 1 to 80 percent by weight and in which the oil phase constitutes from 20 to 99 percent by weight, the oil phase containing at least 10 percent by weight of solid fat.

6. A fatty product according to claim 1, characterized in that it comprises an oil-in-water emulsion in which the water phase constitutes from 1 to 80 percent by weight and in which the oil phase constitutes from 20 to 99 percent by weight.

7. A process for the production of a non-liquid fatty product containing an inert gas, at least one polyunsaturated fatty acid, water and

optionally an antioxidant, wherein the inert gas is whipped into an oil-in-water emulsion or a water-in-oil emulsion wherein the oil phase comprises a mixture of fatty substances which was initially softened by heating and wherein the product thus produced is cooled, c h a r - a c t e r i z e d in using a mixture of fatty substances containing at least 1 percent by weight of a polyunsaturated fatty acid of the n-3 series comprising at least four double bonds and/or at least 0.5 percent by weight of a polyunsaturated fatty acid of the n-6 series comprising at least 3 double bonds and at least 1 percent by weight of oxygen-deficient water.

8. Process according to claim 7, c h a r a c t e r i z e d in using a mixture of fatty substances containing at least 0.5 percent by weight of polyunsaturated fatty acids of the n-6 series comprising at least 3 double bonds, preferably γ-linolenic acid.

9. Process according to claim 7, c h a r a c t e r i z e d in using a mixture of fatty substances containing from about 10 to about 85 percent by weight of refined fish oil.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/DK 91/00017

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: A 23 D 7/00, 02

## II. FIELDS SEARCHED

Minimum Documentation Searched[7]

| Classification System | Classification Symbols |
|---|---|
| IPC5 | A 23 D |

Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in Fields Searched[8]

SE,DK,FI,NO classes as above

## III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

| Category * | Citation of Document,[11] with indication, where appropriate, of the relevant passages[12] | Relevant to Claim No.[13] |
|---|---|---|
| P,A | EP, A1, 0395569 (KATBORG, JON) 31 October 1990, see the whole document -- | 1-9 |
| A | EP, A1, 0319360 (VERNIN, JEAN-GILLES) 7 June 1989, see the whole document -- | 1-9 |
| A | EP, A2, 0304115 (UNILEVER NV) 22 February 1989, see the whole document -- | 1-9 |
| A | US, A, 4764392 (YASUFUKU ET AL) 16 August 1988, see the whole document -- | 1-9 |
| A | EP, A2, 0285198 (UNILEVER NV) 5 October 1988, see the whole document -- | 1-9 |

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## IV. CERTIFICATION

| Date of the Actual Completion of the International Search | Date of Mailing of this International Search Report |
|---|---|
| 19th April 1991 | 1991 -04- 24 |
| **International Searching Authority** | **Signature of Authorized Officer** |
| SWEDISH PATENT OFFICE | Kerstin Boije Janson |

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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

| Category * | Citation of Document, with indication, where appropriate, of the relevant passages | Relevant to Claim No |
|---|---|---|
| A | FR, A, 573718 (M. PETER MÖLLER HEYERDAHL)<br>28 June 1924,<br>see the whole document<br>-- | 1-9 |

# ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.PCT/DK 91/00017

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the Swedish Patent Office EDP file on 91-03-23
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| Patent document cited in search report | Publication date | Patent family member(s) | | Publication date |
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| FR-A- 573718 | 24-06-28 | NONE | | |